(54) Title: UNSATURATED α-OLEFIN COPOLYMERS AND METHOD FOR PREPARATION THEREOF

(57) Abstract

Disclosed are unsaturated α-olefin/α,ω-diene copolymers, and a method of preparation thereof. The copolymers are generally crystalline, free of gel and cross-links, and contain unsaturated side chains and long chain branching. The copolymers contain up to 5 mole percent diene incorporated therein, and may be prepared by copolymerization using a solid-phase, insoluble coordination catalyst, without a solvent, and below the crystalline melting point of the copolymer.

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UNSATURATED α-OLEFIN COPOLYMERS AND METHOD FOR PREPARATION THEREOF

Field of the Invention

This invention relates to copolymers of α-olefins and α,ω-dienes, and a method for their preparation. More particularly, the invention relates to
5 crystalline, gel-free, long chain branched and unsaturated α-olefin/α,ω-diene copolymers and their preparation.

Relevant Art

Selected dienes have been copolymerized with α-
10 olefins in order to introduce unsaturation into the polymer as a site for chemical reactions such as cross-linking. In U. S. Patent 3,658,770 to Longi et al, it is taught that these dienes should be non-conjugated and should have two different kinds of double bonds,
15 the first double bond being copolymerizable with the α-olefin and the second double bond being non-copolymerizable by Ziegler-type catalysts. Thus, useful classes of dienes for introduction of unsaturation into ethylene-propylene terpolymers are
20 straight-chain and branched-chain acyclic dienes, single ring alicyclic dienes, and multi-ring alicyclic and bridged ring dienes, wherein one of the double bonds will copolymerize while the second is inert to the catalyst. Such useful dienes are 1,4-hexadiene,
25 dicyclopentadiene and 5-ethylidene-2-norbornene.

The copolymerization of branched 1,4-dienes with ethylene, propylene or 4-methyl-1-pentene is similarly described in U. S. Patent 4,366,296 to Kitigawa et al. While the copolymerization of pr pylene with α,ω-dienes
30 of at least 6 carbon atoms using a Ziegler typ catalyst in a hydrocarbon diluent is taught in U. S. Patent 3,351,621 to Bacskai, the copolymerization has invariably led to a copolymer insoluble in hot

decahydronaphthalene, indicative of the presence of
cross-links and gel.

    U. S. Patent 2,933,480 to Gresham et al, discloses
the copolymerization of α-olefins and diolefins in
5 which both double bonds are terminal to obtain an
elastomeric (non-crystalline) interpolymer. From U. S.
Patents 4,551,503; 4,340,705; and 3,991,262, all to Lal
et al, it is known to prepare interpolymers of C_4-C_{12} α-
olefins with C_8-C_{36} α,ω-dienes using a Ziegler-type
10 catalyst specially treated with hexaalkyl phosphoric
triamides or organophosphate esters. However, the
interpolymers taught in these patents are also
elastomers, and not crystalline thermoplastics.

    U. S. Patent 3,480,599 to Park discloses
15 elastomers made by copolymerizing trienes with α-
olefins.

    As far as applicants are aware, there is no prior
art teaching crystalline copolymers of α-olefins such
as propylene with α,ω-diene, wherein the copolymer is
20 essentially gel-free and contains residual reactive
unsaturation. Nor are applicants aware of any prior
art teaching the copolymerization of α-olefins and α,ω-
dienes to produce a crystalline, gel-free copolymer,
wherein the copolymerization is effected without a
25 diluent, below the glass transition temperature of the
copolymer product, and using a solid heterogeneous
catalyst.

Summary of the Invention
    It has been discovered that dienes having two
30 Ziegler-polymerizable double bonds can be copolymerized
with α-olefins to obtain a crystalline structure
without extensive gel formation if the copolymerization
is effected with a Ziegler-type catalyst having an
immobil or insoluble catalyst site under conditions
35 for rapidly immobilizing the polymer chain. Immobile
catalyst sites are, for example, those n the face of

crystals, or on surfac s f solid-supported catalyst.
Th growing polymer chains may be immobilized by
crystallization and/or by copolymerizing near or below
the glass transition temperature of the polymer.

5   In one aspect, the invention provides a method of
preparing a gel-free, unsaturated copolymer of an α-
olefin and an α,ω-diene. The method comprises charging
to a reaction zone α-olefin having from 2 to about 12
carbon atoms, α,ω-diene having from 7 to about 30
10 carbon atoms, and solid heterogeneous coordination
catalyst. The method also includes maintaining the
reaction zone essentially free of solvent and at a
temperature at which the α-olefin is fluid but below
the crystalline melting point of the copolymer,
15 effective to produce an essentially gel-free copolymer
with unsaturation.

          In another aspect, the invention provides an
unsaturated crystalline α-olefin copolymer. The
copolymer comprises α-olefin interpolymerized with from
20 0.01 to 5 mole percent of an α,ω-diene having from 7 to
about 30 carbon atoms to produce an unsaturated
crystalline copolymer essentially free of gel. The
copolymer of this invention incorporates the α,ω-diene
comonomer in two different ways. First, one end of the
25 diene comonomer may be reacted in the α-olefin backbone
leaving the other end unreacted to provide unsaturated
side chains. Second, the other end of the diene
comonomer may react with additional monomer to provide
long side chain branches greater in length than the
30 α,ω-diene, in a fashion analogous to the branching in
low density polyethylene (LDPE) which is also sometimes
referred to as branched polyethylene or high pressure
polyethylene. The predomination f either manner of
diene comonomer incorporation can be effect d by the
35 selection of catalyst and polymerization conditions,
and the copolym r properties tailored accordingly. The
side chain unsaturation, for exampl , imparts gamma

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radiation stability and reactive functi nal sites for chemical modification, whereas long chain branching imparts greater melt strength and elasticity to facilitate processing the copolymer in heretofore
5   difficult polypropylene applications such as, for example, blow molding, stretch blow molding, extrusion into pipe, extrusion coating, and high temperature flexural modulus retention. Surprisingly, however, the α-olefin-α,ω-diene copolymer is free of xylene-
10   insoluble gel, regardless of which type of diene incorporation predominates.

Detailed Description of the Invention

The present invention involves the reaction of an α-olefin with an α,ω-diene. Suitable α-olefins
15   include, for example, ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 1-octene, 1-decene, 1-undecene, 1-dodecene and the like. Of these, ethylene, propylene, butene-1, pentene-1, and 4-methyl-
20   1-pentene are preferred, and propylene is particularly preferred. In addition, mixtures of these α-olefins which result in crystalline polymers may also be used, such as, for example, propylene and a minor proportion of ethylene. The invention is described below with
25   reference to propylene as an example of the α-olefin for the sake of brevity and clarity with the understanding that other α-olefins are also contemplated.

Suitable α,ω-dienes contain at least 7 carbon
30   atoms and have up to about 30 carbon atoms, with from 8 to 12 carbon atoms being preferred. Representative examples of such α,ω-dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-d decadi ne, 1,12-tridecadiene, 1,13-
35   tetradecadien , and the like. Of these, 1,7-octadiene,

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and 1,9-d cadiene are preferred, particularly 1,9-decadiene.

The α,ω-diene may comprise from about 0.01 to about 5 mole percent of the copolymer, preferably from about 0.05 to about 2 mole percent, and especially from about 0.1 to 1 mole percent. The diene content can be estimated, for example, by measuring absorbance at 722 cm^{-1} using infrared spectroscopy. Depending upon the catalyst, polymerization conditions and comonomer selection, the copolymer may incorporate unsaturated comonomer side chains comprising from about 0.001 to about 5 mole percent of the copolymer, preferably from about 0.01 to about 2 mole percent, and especially from about 0.1 to about 1 mole percent.

In sharp contrast to the prior art diene copolymers, however, the present copolymer is essentially gel-free and generally crystalline. The absence of gel and cross-links in the present copolymer is evidenced by, for example, very low (less than 0.1 weight percent) or undetectable xylene-insoluble fractions. Also, the high crystallinity of the present copolymers is evidenced by a relatively high hot n-heptane insolubles (HI) fraction, preferably at least 80 weight percent up to as much as 95 weight percent or more. Further, the present copolymers are branched and may have a branching index from about 0.2 to about 0.9, preferably from 0.6 to 0.8. As used herein, the branching index is defined as the ratio of the intrinsic viscosity of the α,ω-diene-α-olefin copolymer to the intrinsic viscosity of the poly-α-olefin homopolymer having the same molecular weight distribution as the copolymer. The copolymer may have any molecular weight suitable for its intended end use, and in th case of polypropylene copolymers, preferably has a melt flow rate (MFR) of from about 0.01 to about 2000, mor preferably from about 0.1 to about 300 and esp cially from about 0.5 to about 70. As used herein,

MFR is d termin d according to ASTM D-1238, conditi n L (2.16 kg, 230°C).

α,ω-Diene-α-olefin copolymers are prepared according to the method of the invention by interpolymerizing the α-olefin and the diene under conditions in which the catalyst site remains relatively insoluble and/or immobile so that the polymer chains are rapidly immobilized following their formation. Cross-link formation through the unsaturation remaining at the free-end of the branch chain resulting from incorporation of the diene into the copolymer is thus inhibited by rapidly immobilizing the otherwise reactive unsaturation site. Such immobilization is effected, for example, by (1) using a solid, insoluble catalyst, (2) conducting the copolymerization in a medium in which the resulting copolymer is generally insoluble, and (3) maintaining the polymerization reactants and products below the crystalline melting point of the copolymer.

Catalysts suitable in the method of the present invention include solid, heterogeneous coordination catalysts, such as Ziegler-type catalysts. An insoluble or otherwise solid-phase catalyst is essential to obtain a gel-free product. Soluble catalysts, such as, for example, the bis-cyclopentadienyltitanium(IV) dichloride-aluminum alkyl system, are generally unsuitable because the second terminal bond of the α,ω-diene is not protected from the catalyst and remains available for reaction in a gel-forming polymerization reaction. Heterogeneous catalysts capable of producing stereo-regular polymers are also preferred, and particularly those catalysts suitable for the preparation of insoluble, isotactic polypropylene. Titanium catalyst containing a minor amount of prepolymerized α-olefin and solid-supported titanium catalysts are particularly preferred. Prepolymerized activated titanium catalyst is described

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in U. S. Patent 4,295,991 to Wrist rs which is hereby
incorporated herein by reference. Briefly, the
prepolymerized activated titanium catalyst is obtain d
by reducing titanium trichloride with an organoaluminum
5 compound at low temperatures, treating the resulting
reduced solid product with about 1-1000 weight percent
α-olefin, and activating the resulting prepolymerized
solid with a halogenated hydrocarbon and a Lewis base
complexing agent or titanium tetrachloride and a Lewis
10 base complexing agent. The prepolymerized activated
titanium catalyst may be employed in combination with
an organometal compound.

   Specific examples of supported titanium catalysts
include: (1) a catalytic solid powder obtained by co-
15 pulverizing a magnesium compound such as magnesium
chloride in an electron donor such as aromatic
carboxylic esters or by reacting these compounds
optionally in the presence of an inert solvent, and
then co-pulverizing the resulting product together with
20 a titanium compound; (2) a pulverulent solid obtained
by reacting a reaction product of a titanium compound
and an electron donor with a magnesium compound by co-
pulverizing the compounds; (3) a pulverulent solid
obtained by reacting a magnesium compound, an electron
25 donor and a titanium compound together through the
simultaneous co-pulverization of these compounds; (4)
a product obtained by supporting titanium tetrachloride
on a co-pulverized product of a solid reaction product
[(hereinafter referred to as a support (I)] of
30 magnesium hydroxychloride and ethylaluminum dichloride
and an aromatic carboxylic acid ester; (5) a product
obtained by co-pulverizing the support (I) and a
complex of an aromatic carboxylic acid ester and
titanium tetrachloride; (6) a product obtain d by
35 treating the co-pulverized product obtained in (5) in a
halogenated hydrocarbon with halide such as halogen,
interhalogen comp und, sulfur monochlorid , sulfur

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dichloride or phosph r us pentachloride; (7) a product obtain d by treating a copulverized product of the support (I) and an ar matic acyl halide with titanium tetrachloride and ethers or an alkoxy compound; (8) a product obtained by treating a copulverized product of the support (I) and an alkoxysilane with titanium tetrachloride and phosphates or phosphites; (9) a product obtained by subjecting a solid product [a support (II)] obtained by reacting the support (I) with a siloxane compound, instead of the support (I), to any procedure described in (4) through (8); (10) a product obtained by using substantially anhydrous magnesium chloride [a support (III)], instead of the support (I), in any procedure described in (4) through (8); (11) a product obtained by adding a halide such as silicon tetrachloride, aluminum trichloride, phosphorus pentachloride, antimony trichloride and tellurium tetrachloride, for example, during the co-pulverization in any procedure described in (4) through (8); (12) a product obtained by adding a siloxyaluminum compound such as trimethylsiloxyaluminumdichloride during the co-pulverization in any procedure described in (4)through (10); (13) a product obtained by adding siloxane compound during the co-pulverization in any procedure described in (4) through (10); (14) a solid obtained by reacting the reaction product of a Grignard compound and a compound containing a Si-H bond, alcohols or phenols, siloxanes, with a compound containing a Si-halogen bond, reacting the resulting solid [a support (IV)] with titanium tetrachloride, and finally reacting the resulting product with a carboxylic acid ester; (15) a solid powder obtained by treating a reaction product of magnesium oxychloride and ethylaluminumdichloride with a polysiloxane, and reacting the resulting product with an alcohol and diethylaluminumchloride in the rder described, and finally reacting the resulting product with titanium

tetrachlorid ;   (16) a solid powder obtained by
r acting magnesium chloride pulverized in a ball mill
with an alkyl titanat and then reacting th resulting
product with titanium tetrachloride and methyl hydrogen
5 polysiloxane; (17) a solid powder obtained by treating
a co-pulverized product of magnesium chloride and
ethoxytrichlorotitanium with iodine trichloride in a
halogenated hydrocarbon; (18) a solid powder obtained
by using magnesium chloride in the procedure described
10 in (15) instead of a compound obtained by treating a
reaction product of magnesium oxychloride and
ethylaluminum dichloride with a polysiloxane; (19) a
solid powder obtained by using a reaction product of
magnesium oxychloride and ethylaluminum dichloride in
15 the procedure described in (16), instead of magnesium
chloride; and the like.   Additional examples of solid-
supported catalysts are described in U. S. Patent
4,366,296 which is hereby incorporated herein by
reference.

20   As mentioned above, the selection of catalyst can
be used to favor the formation of side chain
unsaturation or long chain branching. Generally, the
prepolymerized catalyst has been found to favor more
side chain unsaturation, while the magnesium chloride-
25 supported catalysts tend to favor more long chain
branching.

The copolymerization is effected in gas or liquid
phase, and in the case of propylene, preferably as a
slurry in liquid propylene.   The copolymerization
30 should be in the essential absence of a solvent, which
commonly include pentane, hexane, heptane, octane,
branched alkanes such as those sold under the trade
designation Isopar or the like.   Such solvents tend to
adv rsely affect th copolymer by permitting cross-
35 linking and gel formation to occur which is believed to
result from th solubility of the copolymer ther in and
the ability of the side-chain unsaturation to

participate in a dissolved state in subsequent cross-linking polymerizations. Nonetheless, a very minor proportion of solvent, or a diluent by which the copolymer is not swollen, may permissibly be present in

5 the reactor, e.g. the catalyst may be introduced to the reactor in such a solvent, without significant adverse effects.

The copolymerization reactor temperature must be maintained below the crystalline melting point of the

10 propylene copolymer to facilitate inhibiting the mobility of the unsaturated side chain in participation in additional polymerization reactions which cross-link the polymer to form xylene-insoluble gel. The crystalline melting point of the copolymer is usually

15 in the range of about 155-165°C. The reactor is preferably maintained at from 0° to 100°C, and especially from 30° to 70°C.

In preparing the copolymer, the propylene and α,ω-diene are charged to a suitable reactor vessel with the

20 catalyst. Generally, the propylene in gas or liquid form comprises the bulk of the reactor contents and the diene comonomer(s) may comprise from about 0.001 to about 20 weight percent. If the proportion of diene comonomer feed is too low, insufficient comonomer is

25 incorporated in the resultant copolymer. With an excessive diene comonomer proportion, however, the comonomer can begin to function as a diluent or solvent for the copolymer and gel formation can result. Preferably, the reactor charge comprises from about

30 0.01 to about 20 weight percent of the diene comonomer, especially from about 0.1 to about 10 weight percent.

The reactor charge may also include hydrogen for controlling molecular weight and improving catalyst activity. The hydrogen concentration may be as high as

35 10 m le percent, preferably from about 0.01 to about 5 mole percent, and especially from 1 to 2 mole percent. In general, the more hydrogen present in the reaction

zone, the lower th molecular weight and the gr ater
th catalyst activity. Catalyst is generally f d to
the reactor in suitable amounts to obtain the desired
copolymer production. The reactor may be operated
5 continuously, batch or semi-batch, at a suitable
pressure, usually from about 50 to about 2000 psig,
preferably from about 100 to about 700 psig, and more
preferably from about 300 to about 600 psig.

It is contemplated that the copolymer of the
10 present invention may be used as a reactive feed for
subsequent polymerization reactors, such as, for
example, the ethylene-propylene rubber reactor in a
polypropylene impact copolymer process.

The copolymer is recovered from the reactor and
15 separated from unreacted monomer in a conventional
manner. Because of its novel structure, a wide variety
of end-use applications are contemplated. The side-
chain unsaturation imparts stability to the copolymer
not possessed by homopolypropylene. For example, the
20 propylene-diene copolymer suffers no molecular weight
loss (increased melt flow rate) and forms gel when
treated with peroxide free radical initiators, or when
exposed to gamma radiation, whereas conventional
polypropylene rapidly degrades through a molecular
25 chain scission mechanism and does not form gel. Thus,
the present copolymer may be grafted with vinyl
monomers such as maleic anhydride using peroxide
initiators, or exposed to gamma radiation. This later
application is particularly attractive in medical
30 devices and structures made from or containing the
present copolymer, e.g. syringes, trays and the like,
wherein gamma radiation, typically 2.5-10 MRads, is
used for sterilization purposes. Indeed, such
radiation serves to cross-link the present propylene
35 copolymer via the unsaturation in the side chains,
c nf rring additional dimensional stability n the
medical device or other product.

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The α,ω-diene-propylen cop lymer also has enhanced processability wing to th presence of th long chain branching, in much the same manner that branched polyethylene is known to be easier to process

5 than linear polyethylenes. For example, in food packaging applications wherein the polypropylene container is retorted, e.g. a bottle or dish, the propylene-diene copolymer is easily blow molded or stretch blow molded, whereas conventional polypropylene

10 has such poor melt strength that thin, non-uniform walls are usually obtained in the molded products.

In pipe fabrication, the present propylene-diene copolymers have better processability then conventional polypropylene of equivalent melt flow rate. The

15 copolymer has a lower melt viscosity at a given shear rate because of the long side chains, allowing higher throughput and less sag at the extruder die. Also, the copolymer can be extrusion coated with less neck-in than conventional polypropylene, avoiding the necessity

20 of blending with low density polyethylene as is conventionally done with the propylene homopolymer, and avoiding the concomitantly reduced maximum use temperatures. Moreover, the α,ω-diene-propylene copolymers retain flexural modulus better than

25 conventional polypropylene, allowing the use of the copolymer at higher temperatures in structural applications where the prior art polypropylene would be unsatisfactory.

EXAMPLES

30 In the examples that follow, the catalysts are designated as follows: "catalyst I" is prepolymerized TiCl$_3$ catalyst prepared in accordance with the description in Example 10 of U. S. Patent 4,295,991; and "catalyst II" is prepolymerized MgCl$_2$-supported

35 alkoxysilane-modified TiCl$_4$ catalyst using triethylaluminum as a cocatalyst, wherein the catalyst

is obtained from Mutsui Petrochemical Company under the trade designation SP-101. 1,9-Decadiene from Shell International Chemicals was purified by passage over a column of basic alumina (Baker, Brockman activity 5).

5 The column was 1 inch in diameter and 10 inches high. The diene was collected over activated 4 Å molecular sieves and sparged with nitrogen for 1 hour in order to remove air and water.

1,9-Decadiene contents of the propylene copolymers

10 were measured by infrared spectroscopy. One gram of the copolymer sample was dissolved in 100 ml of xylene. The copolymer-xylene solution was then poured into 500 ml of cold isopropanol. The resulting slurry was filtered and the solid dried under vacuum for 16 hours

15 at 70°C. A 10 mil pad was compression molded at 190°C and this plaque was used for the infrared measurements. Unsaturation in the side chains was determined by measuring the absorbance at 1640 cm^{-1} and the sample thickness and applying the equation:

20
$$X_{unsat} = kA_{1640}/\delta$$

wherein X_{unsat} is the weight percent of unsaturated diene comonomer on the copolymer, k is a constant, A_{1640} is absorbance at 1640 cm^{-1}, and δ is the sample thickness in mm. The total amount of 1,9-decadiene incorporated

25 into the copolymer was also determined by infrared spectroscopy. This was calculated by measuring the absorbance at 722 cm^{-1} and the sample thickness and applying the equation:

30
$$X_{diene} = kA_{722}/\delta$$

wherein X_{diene} is the weight percent of diene comonomer in the copolymer, A_{722} is the absorbance at 722 cm^{-1} and k and δ are as above. The amount of 1,9-decadiene bridging between two polymer chains was determined by

subtracting the amount with terminal unsaturation from the total 1,9-decadiene content. Th unsaturati n content of the polymer was also determined in some cases by high temperature proton nuclear magnetic

5 resonance spectroscopy of the sample dissolved in tetrachloroethane. The mole percentage unsaturation was calculated using the following equation:

$$Y_{unsat} = 100 \ [2A/(B-3A)]$$

wherein Y_{unsat} is the unsaturated diene mole percentage

10 of the sample, A is the integral of the spectrum from 5 to 6 ppm (olefinic region) and B is the integral of the spectrum from 0 to 2 ppm (aliphatic region).

The average molecular weight of the polymers was determined by gel permeation chromatography (GPC). The

15 number of long side chains/molecule for a given weight average molecular weight was then calculated from the number of bridges and the weight average molecular weight.

The melt flow rate (MFR) of the sample was

20 determined by ASTM D-1238, condition L (2.16 kg, 230°C). The heptane insolubles (HI) were determined by measuring the fraction of polymer which remained in an extraction thimble following extraction with refluxing heptane in a Soxhlet extractor under nitrogen for 24

25 hours. The melting point (MP) was determined by differential scanning calorimetry, based on a second melt. Both the heating and cooling rates were 10°C/min.

COPOLYMER PREPARATION AND PROPERTIES

30 **Exampl 1**

A dry, nitrogen-blanketed two-liter autoclave was charg d with 100 ml of 1,9-decadiene; 4 ml of 1 M triethylaluminum; 4 ml of 0.1 M alk xy silane catalyst modifier; hydr gen to 110 psig; and 1250 ml of liquid

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propylene. Th autoclave was continuously stirred and heated to 60°C. Two hundred mg of catalyst I was pressured into the autoclave and polymerization allowed to proceed at 70°C for 1.5 hours. The autoclave was then vented and cooled, and a granular polymer was recovered. The product was placed in a vacuum oven (50°C, 20 mm Hg) overnight. The dried polymer product weighed 261 g. Proton nuclear magnetic resonance spectrometry showed 0.55 mole percent unsaturation, in contrast to polypropylene similarly prepared which contains no measurable unsaturation.

Example 2

Propylene/1,9-decadiene copolymers were produced in two 150 gallon stirred tanks, operated in series, as a reactor. Catalyst I was used. The conditions in the two reactors were as follows:

	REACTOR 1	REACTOR 2
Reaction Temperature (°F)	169.8	159.3
Propylene Flow Rate (lb/hr)	109.9	50.0
1,9-Decadiene Flow Rate (lb/hr)	5.3	2.4
Gas Phase H_2 Concentration (mole %)	3.0	3.3
Solids Concentration (wt %)	29.9	30.2

Sufficient catalyst was fed to produce polymer at a rate of 50.6 lb/hr. Sufficient 15% diethylaluminum chloride (DEAC) in hexane was fed to maintain an Al/Ti ratio of 6.0. The product had a MFR of 27.5 dg/min and an HI of 87.5%. It contained 4.4 ppm Ti. The copolymer had a melting point of 156.6°C and contained 0.30 mole percent 1,9 decadiene unsaturation and 0.50 mole percent total 1,9-decadiene. GPC measurement of the molecular weight distribution in this product gav an M_w = 186,700 and M_w/M_n = 5.26. The measured intrinsic viscosity of th sample was 0.833. The intrinsic viscosity calculated from the GPC data was 1.235. This gave a branching index of 0.674. This

demonstrates that significant branching was present in the copolymer granules from the polymerization reactor. However, the sample contained no gel and was completely soluble in refluxing xylene. The effect of branching was also evident from recoverable compliance measurements of the polymer. The recoverable compliance at 180°C was 6.26 x 10^{-5} cm^2/dyne. Samples of the polymer were injection molded into 125 mil thick bars and subjected to gamma radiation at 1 and 5 MRad dosages. Before irradiation, the gel content was 0%. After irradiation at 1 MRad and 5 MRads, the gel contents were 3% and 34%, respectively. The MFR was also measured on ground injection molded bars, before and after irradiation. Before irradiation, the MFR was 38 dg/min. After irradiation at 1 MRad and 5 MRads, the MFR's were 31 and 2.6 dg/min, respectively. These experiments show that the molecular weight increased due to cross-linking of the polymer after exposure to radiation, in contrast to propylene homopolymers which exhibit severe molecular weight loss with such gamma radiation exposures.

Example 3

Propylene/1,9-decadiene copolymers were produced in the same reactor as described in Example 2. Catalyst system I was used. The conditions in the two reactors were as follows:

	REACTOR 1	REACTOR 2
Reaction Temperature (°F)	169.8	160.2
Propylene Flow Rate (lb/hr)	110.0	50.0
1,9-Decadiene Flow Rate (lb/hr)	7.9	3.6
Gas Phase H$_2$ Concentration (mole %)	1.5	1.7
Solids Concentration (wt %)	33.6	33.1

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Sufficient catalyst was fed to produce polymer at a
rate of 56.7 lb/hr. Sufficient 15% DEAC in hexane was
fed to maintain an Al/Ti ratio of 4.7. The product had
a MFR of 4.2 dg/min and an HI of 90.0%. It contained
5 · 7.2 ppm Ti. The polymer had a melting point of 157.9°C
and contained 0.10 mole % 1,9-decadiene unsaturation
and 0.50 mole percent total 1,9-decadiene. GPC
measurement of the molecular weight distribution in
this product gave a weight average molecular weight
10 (M_w) of 250,000 and ratio of number average molecular
weight (M_n) to M_w of 5.40. The intrinsic viscosity of
the sample was 1.114. The intrinsic viscosity
calculated from the GPC data was 1.580. This gave a
branching index of 0.705. Significant branching was
15 present in the polymer granules from the polymerization
reactor. The gel content of the sample was 0.0%. The
recoverable compliance at 180°C was 6.56 x 10^{-5}
cm^2/dyne. Samples of the polymer were injection molded
into 125 mil thick bars and subjected to gamma
20 radiation. Before irradiation, the gel content was 0%.
After irradiation at 1 MRad and 5 MRads, the gel
contents were 19% and 43%, respectively. The MFR was
measured on ground injection molded bars, before and
after irradiation. Before irradiation, the MFR was 8
25 dg/min. After irradiation at 1 MRad, the MFR was 2
dg/min. After exposure to 5 MRads of radiation, the
sample MFR could not be measured since it would not
flow through an orifice. These experiments show that
the molecular weight increased due to cross-linking of
30 the polymer after exposure to radiation.

Example 4

Propyl ne/1,9-decadiene copolymers were produced
in th sam reactor as described in Example 2.
Catalyst system I was used. The conditi ns in the two
35 r actors were as f llows:

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	REACTOR 1	REACTOR 2
Reaction Temperature (°F)	169.8	159.4
Propylene Flow Rate (lb/hr)	110.0	50.0
1,9-Decadiene Flow Rate (lb/hr)	7.2	3.3
Gas Phase H_2 Concentration (mole %)	1.8	1.9
Solids Concentration (wt %)	30.6	33.4

Sufficient catalyst was fed to produce polymer at a rate of 56.9 lb/hr. Sufficient 15% DEAC in hexane was fed to maintain an Al/Ti ratio of 4.7. The product had a MFR of 7.0 dg/min and an HI of 89.0%. It contained 6.8 ppm Ti. The polymer had a melting point of 158.1°C and contained 0.10 mole percent 1,9-decadiene unsaturation and 0.50 mole percent total 1,9-decadiene.

Comparative Example 1

A commercial propylene homopolymer with an MFR of 1.6 dg/min was irradiated at different dosages to demonstrate the degradation that results when propylene homopolymers are subjected to gamma radiation. The samples were injection molded into 125 mil Izod impact bars and subjected to gamma radiation. After 2.1 MRads the MFR increased to 8 dg/min, at 5.6 MRads the MFR increased to 20 dg/min, and after 10.6 MRads the MFR was 78 dg/min. No cross-linking was observed.

Comparative Example 2

A propylene/hexene copolymer with an MFR of 2.5 dg/min was irradiated at different dosages to demonstrate that severe degradation results when propylene copolymers with other α-olefins are subject to gamma radiation. After 2.1 MRads the MFR increased to 10 dg/min. and at 5.6 MRads the MFR increas d to 39 dg/min.

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Comparativ Example 3

A propylene h mopolymer with a MFR of 15 dg/min
was irradiated at different dosages to demonstrate the
degradation that results when propylene homopolymers
5   are subjected to gamma radiation. The samples were
injection molded into 125 mil Izod impact bars and
subjected to gamma radiation. Before irradiation the
gel content of the sample was 0.0%. After irradiation
at 2.1 MRads, 5.6 MRads, and 10.6 MRads the gel content
10   was 0.0%. No cross-linking was observed.

Comparative Example 4

This example demonstrates the low recoverable
compliance that is observed for polypropylene
homopolymers. The recoverable compliance of a
15   homopolymer having a MFR of 8 dg/min was measured at
180°C. The recoverable compliance was 2.80×10^{-5}
$cm^2/dyne$. This demonstrates the lower elasticity of
the melt for a linear homopolymer.

The foregoing description of the invention is
20   illustrative and explanatory only. Various
modifications will occur to the skilled artisan in view
thereof. All such variations which are within the
scope or spirit of the appended claims are intended to
25   be embraced thereby.

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Claims:

1. An α-olefin/α,ω-diene copolymer, comprising:

   an α-olefin having from 2 to about 12 carbon atoms, interpolymerized with from 0.01 to 5 mole percent of an α,ω-diene having from 7 to about 30 carbon atoms, to produce an unsaturated crystalline copolymer essentially free of gel.

2. The copolymer of claim 1, wherein the α-olefin comprises propylene.

3. The copolymer of claim 1, comprising from about 0.05 to about 2 mole percent of said α,ω-diene.

4. The copolymer of claim 1, comprising from abut 0.001 to about 5 mole percent of unsaturated α,ω-diene.

5. The copolymer of claim 1, wherein the α,ω-diene has from 8 to 12 carbon atoms.

6. An unsaturated propylene/α,ω-diene copolymer, comprising:

   propylene interpolymerized with from 0.01 to 5 mole percent of an α,ω-diene having from 8 to 12 carbon atoms, wherein the copolymer contains unsaturated side chains, is essentially crystalline and is essentially free of gel.

7. The copolymer of claim 6, wherein said copolymer comprises from about 0.05 to about 2 mole percent of said α,ω-diene.

8. The copolymer of claim 6, wherein said copolymer comprises from about 0.001 to about 5 mole percent unsaturated side chains.

9. The copolymer of claim 6, wherein copolymer further includes a minor proportion of ethylene.

10. The copolymer of claim 6, wherein the diene comprises 1,9-decadiene.

11. The c mposition f claim 6, wherein said copolym r
    has a xylen -insolubl fraction of not more than
    0.1 weight percent.

12. The composition of claim 6, wherein said copolymer
    has a heptane-insoluble fraction of at least 80
    weight percent.

13. The composition of claim 6, wherein said copolymer
    has a branching index of from about 0.2 to about
    0.9.

14. The copolymer of claim 6, wherein the copolymer is
    prepared   by   polymerization   with   a   solid
    heterogeneous   catalyst   for   stereoregular
    polymerization   at   a   temperature   below   the
    crystalline   melting   point   of   the   copolymer
    essentially in the absence of a solvent.

15. A propylene/decadiene copolymer, comprising:
        propylene copolymerized with from 0.01 to 5
            mole percent total 1,9-decadiene and
            from about 0.001 to about 5 mole percent
            unsaturated 1,9-decadiene wherein the
            copolymer has less than 0.1 weight
            percent of xylene-insolubles, at least
            80 weight percent heptane insolubles and
            a branching index of about 0.2 to about
            0.9.

16. The copolymer of claim 15, comprising from 0.01 to
    2 mole percent total 1,9-decadiene.

17. The copolymer of claim 15, comprising from 0.01 to
    2 mole percent unsaturated diene.

18. The copolymer of claim 15, comprising from 80 to
    95 weight percent heptane insolubles.

19. The copolymer of claim 15, wherein the copolymer
    has a branching index of from about 0.6 to about
    0.8.

20. A method for preparing a gel-fre unsaturated copolymer of an α-olefin and an α,ω-diene, comprising:

charging to a reaction zone an α-olefin having from 2 to about 12 carbon atoms, from 0.01 to 20 weight percent of an α,ω-diene having from 7 to about 30 carbon atoms, and a solid heterogeneous coordination catalyst;

maintaining the reaction zone essentially free of solvent and at atemperature at which the α-olefin is fluid but below the crystalline melting point of the copolymer, effective to produce an essentially gel-free, linear copolymer with unsaturation.

21. The method of claim 20, wherein the α-olefin is selected from ethylene, propylene, butene-1, pentene-1 and 4-methyl-1-pentene.

22. The method of claim 20, wherein the α,ω-diene has up to 12 carbon atoms.

23. The method of claim 20, wherein the catalyst is a Ziegler-type catalyst.

24. The method of claim 20, wherein up to 10 mole percent hydrogen is charged to said reaction zone to control molecular weight of said copolymer.

25. The method of claim 20, wherein the copolymer has from 0.1 to 1 mole percent unsaturation.

26. A method for preparing a gel-free, unsaturated copolymer of an α-olefin and an α,ω-diene, comprising:

charging an α-olefin selected from ethylene, propylene, butene-1,pentene-1 and 4-methyl-1-p ntene to a reaction zone with from 0.01 t 20 weight percent f an α,ω-diene f from 7 to 12 carb n atoms, up to 10 mole percent hydrogen, and a

        solid,   h terogeneous   Ziegler-type
        catalyst;

      maintaining the reaction zone essentially
        free of solvent and at atemperature at
        which the α-olefin is fluid but
        substantially below the crystalline
        melting point of the copolymer; and

     recovering an essentially linear and gel-free
        copolymer from the reaction zone,
        wherein the copolymer has from 0.1 to 1
        mole percent unsaturation.

27. The method of claim 26, wherein the α-olefin is propylene.

28. The method of claim 26, wherein the α,ω-diene comprises 1,9-decadiene.

29. The method of claim 26, wherein the catalyst is a solid-supported catalyst.

30. The method of claim 26, wherein the catalyst is obtained by (1) contacting TiCl₄ with an organoaluminum compound at a temperature between about -50° and 30°C to produce a TiCl₃ reduced solid product, (2) contacting the reduced solid TiCl₃ product with a minor amount of an α-olefin having at least 3 carbon atoms under polymerization conditions to obtain a reduced TiCl₃ solid product containing between about 1 and 1000 weight percent of prepolymerized α-olefin based on the weight of TiCl₃, and (3) treating said prepolymerized reduced solid with one of (a) a chlorinated hydrocarbon having at least 2 carbon atoms and a Lewis base complexing agent or (b) TiCl₄ and a Lewis base complexing agent, to convert the prepolymerized TiCl₃ reduced solid to a substantially n n-friable highly active, crystalline pr polymeriz d TiCl₃ composition.

31. The method of claim 30, wherein the catalyst further compris s an organom tallic cocatalyst.

32. A method of preparing an isotactic, essentially
    g l-free copolymer of propylene and an α,ω-diene
    comprising:

    charging propylene, from 0.01 to 20 weight
    percent 1,9-decadiene, from 0.01 to 5
    mole percent hydrogen, and a solid
    heterogeneous Ziegler-type catalyst for
    isotactic polymerization, to a reaction
    zone;

    maintaining the reaction zone essentially
    free of solvent and at a temperature
    below about 150°C effective to randomly
    copolymerize said propylene and said
    diene; and

    recovering an essentially gel-free isotactic
    copolymer.

33. The method of claim 32, wherein a minor proportion
    of ethylene is charged to said reaction zone.

34. The method of claim 32, further comprising
    polymerizing said copolymer with ethylene and
    propylene in another rection zone.

35. The method of claim 32, wherein said catalyst is
    obtained by (1) contacting TiCl₄ with an
    organoaluminum compound at a temperature between
    about -50° and 30°C to produce a TiCl₃ reduced
    solid product, (2) contacting the reduced solid
    TiCl₃ product with a minor amount of an α-olefin
    having at least 3 carbon atoms under
    polymerization conditions to obtain a reduced
    TiCl₃ solid product containing between about 1 and
    1000 weight percent of prepolymerized α-olefin
    based on the weight of TiCl₃, and (3) treating
    said prepolymerized reduced solid with one of (a)
    a chlorinated hydrocarbon having at least 2 carbon
    atoms and a Lewis base complexing agent or (b)
    TiCl₄ and a Lewis base c mplexing agent, to
    conv rt th prepolymerized TiCl₃ reduced s lid to

a   substantially   n n-friable   highly   active,
crystalline prepolymerized TiCl$_3$ composition.

36. The method of claim 35, wherein the catalyst
includes an organometallic cocatalyst.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5   C 08 F 210/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	C 08 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	CHEMICAL ABSTRACTS, vol. 71, no. 5, 8 September 1969, (Columbus, Ohio, US), see page 23, abstract no. 39638e, & JP-A-69 06 275 (MITSUI CHEMICAL INDUSTRY CO., LTD) 17 March 1969, see the abstract	1-9
A	EP-A-0 317 240 (MITSUI) 24 May 1989, see the claims	1,10
A	US-A-3 351 621 (R. BACSKAI) 7 November 1967, see the whole document (cited in the application)	1,10
A	EP-A-0 219 166 (STAMICARBON) 22 April 1987, see the whole document	1,10

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

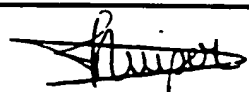| Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12-08-1991	1 6 SEP 1991

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	Mme N. KUIPER

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 10/09/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		AU-B-	608094	21-03-91
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		US-A-	4868264	19-09-89